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Mechanism of Reaction and Photoacid Generation of 1,2-di(Arylsulfonyl)hydrazine PAGs: A Laser Flash Photolytic Study

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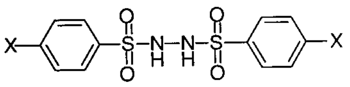
The photochemical behavior of four 1,2-di(arylsulfonyl)hydrazine photoacid generators has been studied by means of nanosecond laser flash photolysis ($\lambda = 266$ nm) and steady-state photolysis ($\lambda = 254$ nm) with the aim of understanding the reactions involved in photoacid generation. Upon photoexcitation, homolytic cleavage of the S−N bond results in the formation of arylsulfonyl radicals. The nitrogen-centered radical that also results from this cleavage decomposes to yield another arylsulfonyl radical. The arylsulfonyl radical generates acid via reaction with oxygen to yield a peroxysulfonyl radical, which subsequently reacts with a hydrogen donor to yield a peroxysulfonic acid. The sulfonic acids detected in product studies are presumed to be the stable decomposition products of these peroxysulfonic acids. Desulfonylation of the arylsulfonyl radical to generate SO_2 is a very minor pathway that occurs in competition with acid generation. Photoacid generation quantum yields upon laser excitation were found to range from 0.05 to 0.1.

Introduction

Photoacid generators (PAGs) are employed by the microlithographic industry in the preparation of chemically amplified photoresist materials. The role of photogenerated acid in photoresists is to catalyze deblocking or cross-linking chemistry in the polymeric resist material, thereby allowing for the subsequent development of a pattern in the resist.[1−4] The study of the possible reactions that PAGs undergo upon photoexcitation is important to gauge their potential for practical applications and to determine their efficiency as acid generators. This knowledge is becoming increasingly important as the microlithographic community shifts to 193-nm lithography for which the design of new PAGs will likely be required.

The PAGs currently under consideration are 1,2-di(arylsulfonyl)hydrazines, which are very similar in structure to arylsulfonamides whose photochemistry has already been described, in part because of the utility of the arylsulfonamides as photolabile protecting groups for amines.[5] Product studies on arylsulfonamides suggest that the main pathway for photodecomposition is homolytic cleavage of the S−N bond to yield an arylsulfonyl radical in addition to a nitrogen-centered radical.[6] In light of the similarity between arylsulfonamides and 1,2-di(arylsulfonyl)hydrazines, one might anticipate similar photochemical behavior for the latter.

The mechanism of the photoreaction of a set of 1,2-di(arylsulfonyl)hydrazines (**1a**−**d**) has been established by laser flash photolysis (LFP) and steady-state techniques. The photoacid generation quantum yields (Φ_{acid}) of **1a**−**d** under laser irradiation at 266 nm have been determined. Additionally, for **1d**, the quantum yield of decomposition of PAG (Φ_{decomp}), and the quantum yield of *p*-chlorobenzenesulfonic acid formation (Φ_{ClSOH}) under steady-state irradiation at 254 nm have also been determined. This study has been aided greatly by previous work in this lab with *N*-oxysuccinimidoarylsulfonate PAGs (**2a**−**d**), for which many mechanistic similarities were found, that appears in the preceding paper in this issue.[7]



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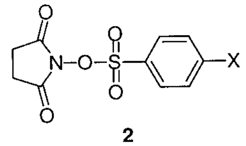

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1a,2a X = H
1b,2b X= CH_3
1c,2c X=Fl
1d,2d X=Cl

Experimental Section

Materials. 1a−**d** were prepared by the reaction of hydrazine hydrate (1 equiv) with the corresponding arylsulfonyl

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chloride (2 equiv) in a manner similar to that described in the literature for analogous compounds.[8] Chemical purities were determined by HPLC, and NMR spectra were measured at 400 MHz in DMSO.

1a: mp 215.9 °C; purity 99.8%; ^{1}H NMR δ 9.74 (s, 2H, N−H), 7.76 (m, 4H), 7.67 (m, 2H), 7.59 (m, 4H); ^{13}C NMR δ 139.15, 134.27, 130.14, 128.71. **1b**: mp 216.4 °C; purity 100%; ^{1}H NMR δ 9.58 (s, 2H, N−H), 7.62 (m, 4H), 7.38 (m, 4H), 2.38 (s, 6H); ^{13}C NMR δ 144.70, 136.26, 130.53, 128.78. **1c**: mp 203.0 °C; purity 99.8%; ^{1}H NMR δ 9.80 (s, 2H, N−H), 7.84 (m, 4H), 7.45 (m, 4H); ^{13}C NMR δ 165.75, 135.50, 131.95, 117.30. **1d**: mp 207.7 °C; purity 99.9%; ^{1}H NMR δ 9.86 (s, 2H, N−H), 7.75 (m, 4H), 7.68 (m, 4H); ^{13}C NMR δ 139.29, 137.89, 130.75, 130.31.

Anthracene (zone-refined, >99%), potassium iodide (99%), potassium iodate (99.5%), sodium tetraborate decahydrate (≥99.5%), *p*-toluenesulfonic acid monohydrate (98.5%), and poly(methyl methacrylate) were obtained from Aldrich and used as received. Tetrabutylammonium chloride was purchased from Fluka (>99%) and used without further purification. *p*-Chlorobenzenesulfonic acid (ClSOH, 90%) was supplied by Aldrich and recrystallized from ethanol/water. 2-Methyl-4,6-bis(trichloromethyl)-1,3,5-triazine (MTT) was purchased from Panchim and purified by recrystallization from methanol (2 times) and subsequent sublimation. Rhodamine B base (Rb) was obtained from Aldrich and purified by column chromatography on silica gel (230−400 mesh) using acetone as the eluent. The spectroscopic quality of the dye was then verified by means of fluorescence excitation spectroscopy.

Acetonitrile, tetrahydrofuran, and 2-methoxyethyl ether (diglyme) were all OmniSolv-grade solvents from BDH and used as received. 2-Propanol, HPLC-grade from Sigma-Aldrich, was used as received.

General Techniques. Ground-state absorption spectra were recorded using a Varian Cary 1E spectrophotometer. Suprasil quartz cells with a 10-mm optical path were employed in these experiments.

For the LFP, the fourth harmonic (λ = 266 nm) from a Surelite Nd:YAG laser (<10 ns pulse width, ~20 mJ/pulse) and occasionally an excimer laser at 308 nm were used for excitation. The system was controlled by a Power Macintosh computer running LabVIEW 4.1 software (National Instruments). A Tektronix 2440 digital oscilloscope was used to digitize the photomultiplier signal. Suprasil quartz cells (7 × 7 mm) were used in these experiments. Further details of a similar laser system have been provided elsewhere.[9,10]

Steady-state irradiations were performed in a photoreactor equipped with RPR-2540 and RPR-3500 lamps. Quartz cells of the same type as those for LFP were used and rotated by means of a "merry-go-round" apparatus to ensure that all the samples received the same irradiation dose.

Product studies on these steady-state irradiations were performed on a HPLC (Varian 9010 pump with a model 9065 autosampler and a model 9090 diode array detector interfaced to a 386 computer equipped with Star Workstation software) employing a 25-cm Zorbax C-18 column with a 25:75 water/methanol mobile phase. Products were further characterized by LC/MS analysis in a Millennium system using a reverse-phase column and a combination of UV diode array and mass spectroscopic detection.

Thin polymer films were spin coated at 3000 rpm for 20 s onto 2.5-cm quartz disks using an Integrated Technologies Inc. P-6000 spin coater. The coating solution was 15 wt % PMMA in diglyme. To this coating solution was added a PAG (~5 wt % relative to solids). The films were baked at 90 °C for 5 min immediately after coating.

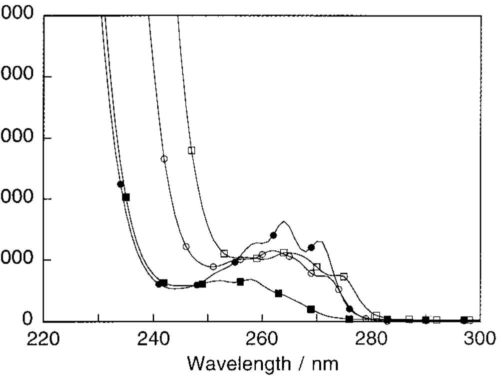

Figure 1. Ground-state absorption spectra of (●) **1a**, (○) **1b**, (■) **1c**, and (□) **1d** in acetonitrile solutions.

Measurement Conditions. The conditions under which LFP experiments, as well as quantum yield determinations, were performed are identical to those described in the preceding paper in this issue.[7]

The relative yields of arylsulfonyl radical formation were determined via LFP by measuring the absorbance change (ΔO.D.) at 470 nm, where only the arylsulfonyl radical absorbance contributes to the observed signal. This measurement was taken 100 ns following the laser pulse, before significant decay of the signal occurred, for **1b** and **1d** at various laser powers. For purposes of comparison, similar measurements were performed with **2b** and **2d**. A comparison of the slopes of the linear plots between PAGs that generate the same arylsulfonyl radical, i.e., **1b** with **2b** and **1d** with **2d**, gives a relative yield of the amount of arylsulfonyl radical generated within the laser pulse. The yields can only be stated relative to another molecule that yields the same arylsulfonyl radical because the extinction coefficients of these species are not known.

Results and Discussion

The ground-state absorption spectra of **1a−d** in acetonitrile (Figure 1) are very similar with a main peak at <240 nm (log $\epsilon \approx 4.5$) and another weaker band (log $\epsilon \leq 3.3$) extending from 250 to 280 nm.

The transient absorption spectra obtained upon LFP of the PAGs in N_2-saturated acetonitrile also exhibit common features. They all show an intense signal in the UV region and another weaker band in the visible region. The time evolution of the absorption bands in both the UV and visible regions reveals the presence of two transients. The transient absorption spectrum of **1d** appears in Figure 2 and serves as a representative example of this behavior. The longer-lived species decays with first-order kinetics with lifetimes ranging from 130 to 240 μs (Figure 2, inset a) and absorbs primarily in the UV with a tail extending out to 400 nm. There is also a residual absorption in the UV region of the spectrum, evident in the inset of Figure 2, which is presumably due to the formation of photoproducts. The shorter-lived species also decays with first-order kinetics, with lifetimes ranging from 6 to 31 μs and absorbs from 300 to 600 nm. The kinetics can be monitored at 470 nm without interference from the aforementioned absorbing species. (Figure 2, inset b).

To aid in the identification of the shorter-lived transient, experiments with various quenchers were performed on **1a−d**. The observed transient reacts with O_2 to give rate constants ranging from 9.8 × 10^8 to 1.2 ×

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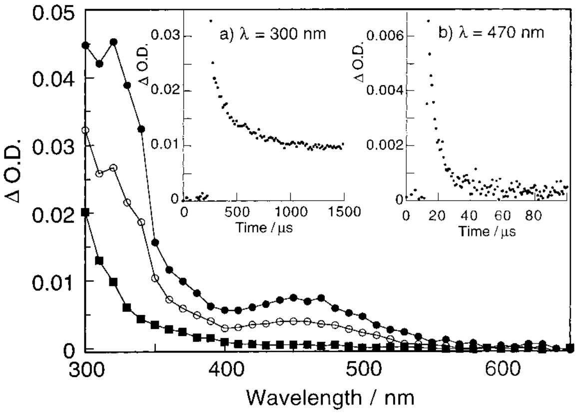

Figure 2. Transient absorption spectrum obtained upon laser flash photolysis of **1d** in N_2-saturated acetonitrile solutions recorded (●) 0.8, (○) 7.2, and (■) 78 μs after the laser pulse. Inset a: Kinetic decay trace monitored at 300 nm. Inset b: Kinetic decay trace monitored at 470 nm.

10^9 M^{-1} s^{-1}, that is, slightly below diffusion-controlled rates, which suggests that it is either a radical or a triplet. There was no effect on the lifetime of the transient in the presence of tetrabutylammonium chloride, anthracene, or the hydrogen donors tetrahydrofuran and 2-propanol. This indicates that the transient is not a cation, triplet, or reactive radical centered on carbon or oxygen. However, because the reactivity of the transient with O_2 indicates that it is a radical species, one is forced to conclude that the observed transient is probably a radical centered on a heteroatom. Judging from the photochemistry of sulfonamides (vide supra) the most likely candidate for this transient is the arylsulfonyl radical. These species were found to be involved in the photodecomposition of **2a**–**d**, which is described in the preceding paper in this issue.[7] As such, the behavior of arylsulfonyl radicals under laser flash photolytic conditions has been extensively described and is consistent with the results obtained in the present study.

In addition to the kinetic data, which suggest that this transient is an arylsulfonyl radical, one must also consider the spectral characteristics of the transient. The absorption spectra of arylsulfonyl radicals have been previously characterized.[11,12] To determine whether these species contribute to the transient absorption spectra obtained in this study, the signal due to the long-lived species and the residual absorption were subtracted from the overall spectrum, which appears in Figure 2. The remaining spectrum (Figure 3), which has a well-defined maximum above 300 nm, is consistent with those appearing in the literature for arylsulfonyl radicals and is tentatively ascribed as such here.

Additional behavior of arylsulfonyl radicals previously observed in this lab is a desulfonylation reaction to yield SO_2 and aryl radicals.[7] This process was detected by LFP via the observation of signals assigned to arylperoxy radicals that are formed in the reaction of aryl

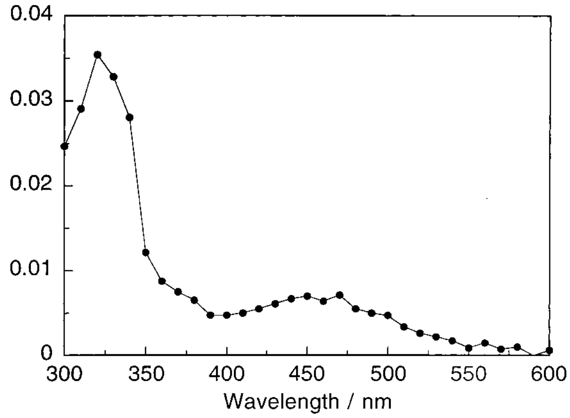

Figure 3. Absorption spectrum assigned to the arylsulfonyl radical obtained from Figure 2 by subtracting the trace obtained 78 μs after the laser pulse from that obtained 0.8 μs after the laser pulse.

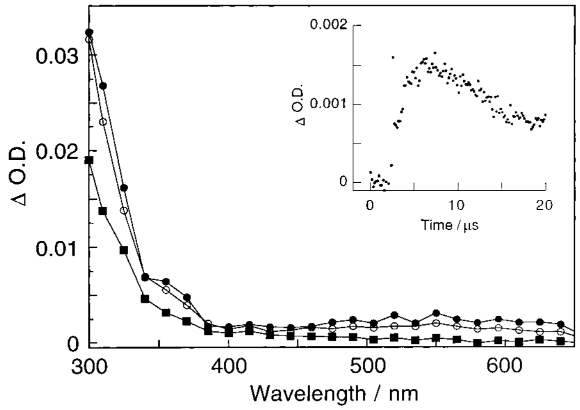

Figure 4. Transient absorption spectrum obtained upon laser flash photolysis of 2d in O_2-saturated acetonitrile solutions recorded (●) 1.2, (○) 6.8, and (■) 78 μs after the laser pulse. Inset: Kinetic trace monitored at 560 nm obtained at a shorter time scale than the accompanying spectrum to observe the growth and decay of the arylperoxy radical.

radicals with O_2.[13–18] This signal consisted of an intense band in the UV region, whose maximum was located below 300 nm, and a second broad band in the visible region, which was centered at 560 nm. The arylperoxyl radical was characterized, in part, by its kinetics of formation (rise time <10 μs) and its subsequent decay on similar time scales. Although such a signal is observed in the photolysis of **1a**–**d** (Figure 4), it is very weak, and we could not perform detailed kinetic analysis (Figure 4, inset). However, in light of the other evidence for the presence of arylsulfonyl radicals, we suggest that the observed species is the arylperoxy radical that forms from the aryl radicals produced via the desulfonylation of the first-formed arylsulfonyl radical. Judging from the LFP studies, the primary photochemical step is

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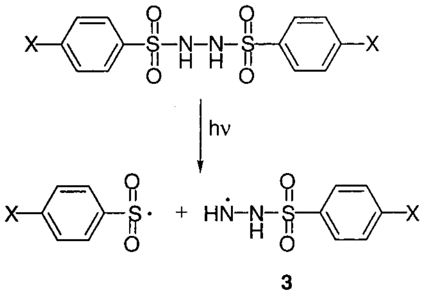
Scheme 1



homolytic cleavage to yield the arylsulfonyl radical and a nitrogen-centered radical (**3**) as shown in Scheme 1.

As such, **3** is a likely candidate for the heretofore unidentified transient signal observed in the LFP experiments. To determine whether **3** is responsible for this transient signal, quenching experiments were again performed. The observed transient was not quenched by O_2, anthracene, *tert*-butylammonium chloride, or 2-propanol. The reactivity of a nitrogen-centered radical derived from an arylsulfonyl-substituted hydrazine, i.e., **3**, is difficult to predict but the behavior displayed by this transient is not inconsistent with its assignment as **3**. Its lack of reactivity with O_2 and 2-propanol can be rationalized by the delocalization of the radical center on both nitrogen atoms.

To better confirm the nature of this transient, we consider the possibility of generating **3** unambiguously via an independent process and comparing the spectral characteristics with those observed in the direct photolysis of **1b**. For this purpose we employed *tert*-butylperoxide as the source of *tert*-butoxy radicals and *p*-toluenesulfonhydrazide as the precursor for **3**. The proposed reaction involves hydrogen-atom abstraction by the *tert*-butoxy radical from the hydrazide to form **3** exclusively. The rate constant for H abstraction was found to be 6.5×10^6 M^{-1} s^{-1}. This value is more than an order of magnitude larger than one would expect for the reaction of *tert*-butoxy radicals with the methyl substituent of a derivative of toluene[19] so it is presumably due to reaction with the hydrazine moiety of the hydrazide. We assume that the radical is formed β to the sulfonyl group because of the greater number of hydrogens available for abstraction and the increased distance between the electrophilic radical center being formed on nitrogen and the electron-withdrawing sulfonyl moiety.

The transient absorption spectra generated during this reaction and during the direct photolysis of **1b** appear in Figure 5 and its inset, respectively. A comparison of the two transients reveals that they are sufficiently similar in lifetimes (<100 μs) and appearance to conclude that the transient observed in the LFP of **1b** is the same as that formed in the reation of *tert*-butoxy radicals with *p*-toluenesulfonhydrazide and has the structure assigned to **3**.

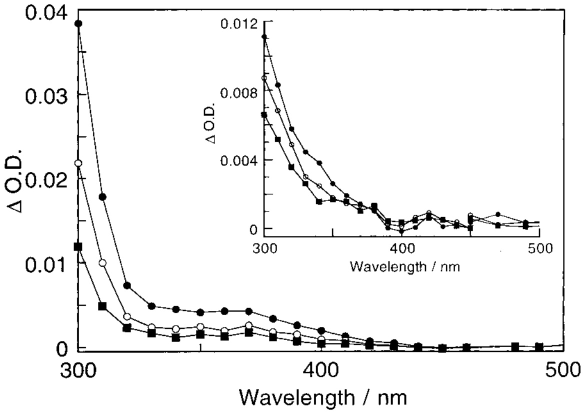


Figure 5. Transient absorption spectra resulting from the LFP at 308 nm of *tert*-butylperoxide in the presence of *p*-toluenesulfonhydrazide to generate the N-centered radical **3** recorded (●) 84, (○) 256, and (■) 628 μs after the laser pulse. Inset: Transient absorption spectra resulting from LFP at 266 nm of PAG **1b** assigned to the N-centered radical **3** recorded (●) 84, (○) 192, and (■) 560 μs after the laser pulse.

Table 1. Φ_{acid} and Arylsulfonyl Radical Yields under LFP Irradiation at 266 nm in Acetonitrile Purged with N_2

PAG	Φ_{acid}	$ArSO_2$[a,b]	$\Phi_{acid}/ArSO_2$	PAG	Φ_{acid}	$ArSO_2$	$\Phi_{acid}/ArSO_2$
1a	0.05			**2a**	0.04		
1b	0.06	0.7	0.08	**2b**	0.04	1.0	0.04
1c	0.1			**2c**	0.05		
1d	0.1	0.9	0.1	**2d**	0.05	1.0	0.05

[a] Arylsulfonyl radical yield. [b] Normalized with corresponding PAG: **2b** or **2c**.

Given the interest in these molecules as PAGs for use in the microlithographic industry, both the amount and type of acids produced are of primary concern. The efficiency of acid generation is an important parameter for determining both the amount of PAG and the appropriate laser dose for catalysis of the required reactions in a resist. The Φ_{acid} values for **1a**–**d** and **2a**–**d** appear in Table 1. Additionally, concerns over acid loss and acid diffusion in resist films prevent the use of PAGs that generate small, volatile acids.[20] It is therefore important to address the manner by which the arylsulfonyl radicals and perhaps **3** generate acid. Product studies reveal that the main photoproducts from **1b** and **1d** are the corresponding sulfonic acids. This result is consistent with the fact that **2a**–**d** also generate sulfonic acids from arylsulfonyl radical intermediates.[7] It was proposed that the sulfonic acid is the stable decomposition product of a first-formed peroxysulfonic acid. The peroxysulfonic acid is formed via the reaction of arylsulfonyl radicals with O_2, followed by hydrogen abstraction. These reactions of the arylsulfonyl radical and previously discussed competive processes appear in Scheme 3. Mechanisms for sulfonic acid generation from arylsulfonyl radicals that do not involve O_2 have also been proposed.[21]

A confirmation of the involvement of O_2 in the acid generation process comes from the fact that the Φ_{acid} value for **1d** measured via LFP in O_2-saturated solution is 0.17, or almost double the value measured in solutions degassed with nitrogen.[22] Residual O_2 in solutions purged with N_2 might be the source of acid in these experiments as evidenced by the fact that a preliminary

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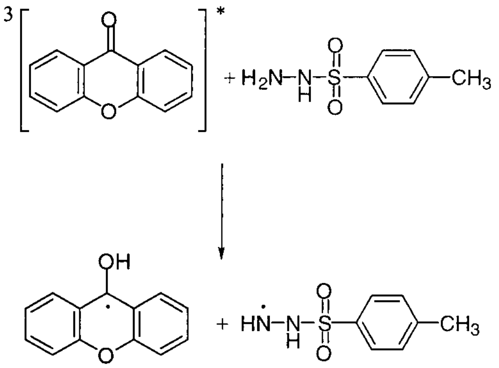
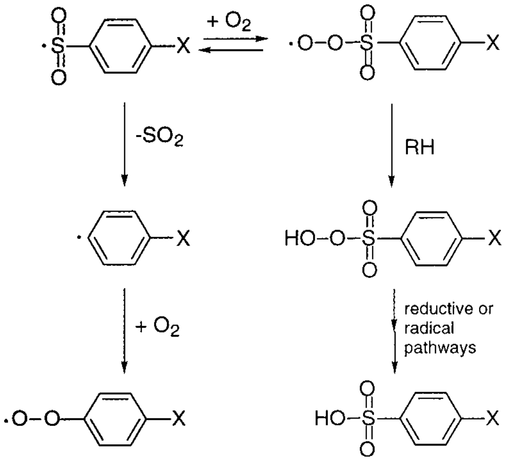
(22) The difference in acid generation efficiency is not a result of a difference in the yields of arylsulfonyl radicals, which are essentially the same in the two solutions.

Scheme 2



Scheme 3



experiment in which more rigorous degassing with Ar instead of N_2 was employed prior to lamp irradiation reduces the yield of acid by a factor of 3 compared to that obtained after purging with N_2 and by a factor of 9 compared to that obtained after purging with O_2.[23] These results clearly indicate that any acid generation pathways that do not involve O_2 make minor contributions to overall acid production.

The potential involvement of **3** in further acid generation via its sulfonyl moiety is an interesting possibility as it allows for the generation of two acid molecules from one PAG molecule. To probe the fate of this fragment, the relative arylsulfonyl radical yields were measured by means of LFP (Table 1) and compared to Φ_{acid}. The Φ_{acid} measurements are based on the protonation of Rb by photogenerated acid, which is accompanied by a dramatic change in its absorption spectra. Details of the experiment have been described elsewhere,[24-26] but here, it should be noted that the protonation of Rb by the photogenerated acid typically occurs over the course of several milliseconds following the laser pulse, and as a result, it can contain contributions from chemical processes that occur long after the primary photochemical step. In contrast, the relative yields of arylsulfonyl radicals for **1b** and **1d** are measured 100 ns following the laser pulse and, hence, contain contributions only from species generated in the primary photochemical step or very quickly thereafter. For purposes of comparison, similar measurements were performed with **2b** and **2c**, the results of which appear in Table 1. **2b** and **2c** were used for comparison because these molecules have only one sulfonyl moiety, whereas **1b** and **1d** contain two such moieties. The interesting result, also shown in Table 1, is that the ratio of Φ_{acid} to the arylsulfonyl radical yield is about twice as large for **1b** and **1d** as for **2b** and **2c**. If one makes the reasonable assumption that arylsulfonyl radicals have the same efficiency for generating acid in both PAG classes, this result indicates that **1b** and **1d** generate twice the amount of acid for a given primary yield of arylsulfonyl radicals. This result clearly indicates that **3** decomposes to yield an acid precursor, and also the factor of 2 suggests that **3** decomposes very efficiently and yields a second arylsulfonyl radical.[27] This arylsulfonyl radical does not contribute to the measured arylsulfonyl radical yields because it results from the decay of **3** at times long after the laser pulse and, hence, long after the arylsulfonyl yields have been determined. Additionally, this extra source of arylsulfonyl radicals does not affect the kinetics observed via LFP because the decay of **3**, which generates the arylsulfonyl radical, is slow relative to the decay of the arylsulfonyl radical itself and therefore its steady-state concentration is very low.

To more directly demonstrate the ability of **3** to generate acid, its formation was sensitized via reaction of *p*-toluenesulfonhydrazide with triplet xanthone ($^3XAN^*$). The bimolecular rate constant for triplet quenching is 9×10^8 M^{-1} s^{-1}, which is too large to be due to the interaction between xanthone and the aryl moiety[28] or to direct hydrogen-atom abstraction from the hydrazide moiety,[29] so it is therefore probably a result of electron/charge transfer followed by proton transfer. The overall reaction is the transfer of a hydrogen atom to $^3XAN^*$, (Scheme 2) as evidenced by the decay of the characteristic signal of $^3XAN^*$ ($\lambda_{max} = 630$ nm) and the appearance of the signal of the xanthone ketyl radical ($\lambda_{max} = 480$ nm, see Figure 6). To determine whether acid is generated after the formation of **3**, we irradiated xanthone (absorbance at 350 nm $\approx$ 0.3) in the presence of 0.018 M hydrazide. This concentration is enough to quench more than 90% of the $^3XAN^*$ formed. Xanthone, rather than *tert*-butoxy radicals, was used to generate **3** in this experiment because the rate constant for the quenching of $^3XAN^*$ by *p*-toluensulfonhydrazide is more than 2 orders of magnitude larger, thereby allowing for more efficient quenching and a concomitant increase in the yield of **3**. Rb was again used as the acid sensor, and a sample of the irradiated solution was added to a stock dye solution. The results of the experiment reveal

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(23) This acid yield experiment was performed in a 7 × 7 mm quartz cell containing 2 mL of solvent as compared to the acid yield experiments performed on the laser system in which as much as 500 mL in a flow system are used. Clearly, the potential for residual O_2 in the solution after degassing, as well as introduction of O_2 during the experiment, is much greater under the conditions in which laser excitation is employed.

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(27) An acid precursor other than the arylsulfonyl radical might have a different efficiency for generation of acid than the arylsulfonyl radical and would therefore not result in a factor of 2 in the values.

(28) Coenjarts, C.; Scaiano, J. C. *J. Am. Chem. Soc.* **2000**, *122*, 3635−3641.

(29) The hydrogen-abstraction ability of xanthone in acetonitrile is similar to that of the *tert*-butoxy radical. See ref 28 and references therein.

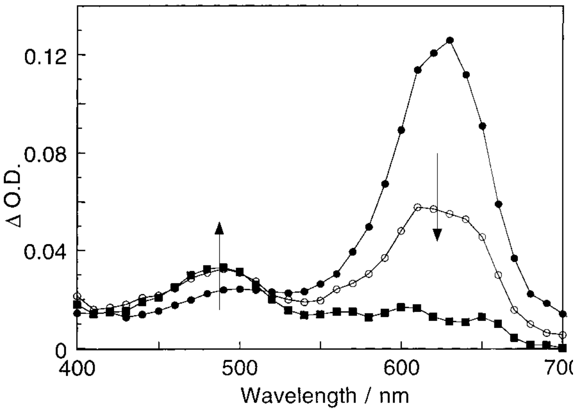

Figure 6. Transient absorption spectrum obtained upon excitation of xanthone in the presence of 0.036 M *p*-toluenesulfonhydrazide taken (●) 8, (○) 40, and (■) 472 ns after the laser pulse.

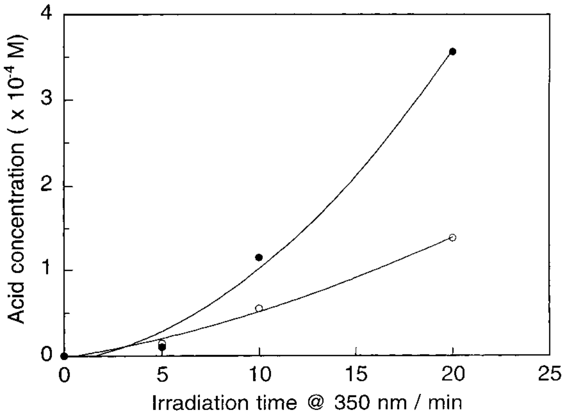

Figure 7. Sensitized acid generation by excitation of XAN in the presence of (●) 0.021 M **1b** and (○) 0.018 M *p*-toluensulfonhydrazide and subsequent detection with Rhodamine B base.

Scheme 4

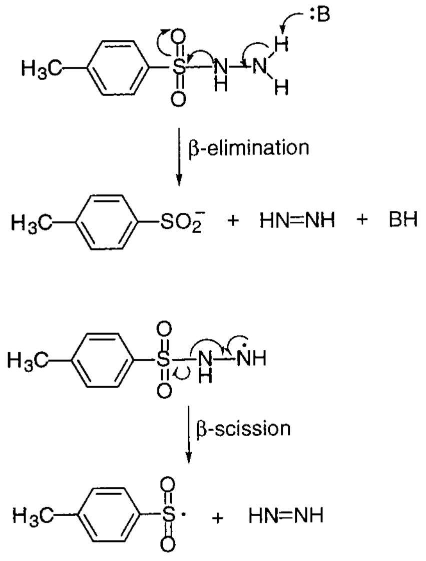

Table 2. Quantum Yield Data for 1d Obtained under Steady-State Irradiation at 254 nm in Acetonitrile Purged with O_2

1d	Φ_{acid}	Φ_{ClSOH}	Φ_{decomp}
H-donor[a]	0.43	0.56	0.28
no H-donor	0.64	0.62	0.27

[a] 0.5 M diglyme.

that sensitized acid formation occurs when xanthone is excited in the presence of *p*-toluenesulfonhydrazide (Figure 7). This result confirms that radical **3** does decompose to yield acid, thereby making a significant contribution to overall acid generation in **1a**–**d**.

To this point, details of the mechanism of decomposition of **3** have not been discussed apart from the fact that it yields an arylsulfonyl radical. Stoichiometry alone suggests that formation of the arylsulfonyl radical is accompanied by the formation of diimide, N_2H_2. Attempts to detect diimide by exploiting its behavior as a reducing agent of alkenes[30] were, not entirely surprisingly, unsuccessful given that the typical conditions for reactions of this type involve large excesses of diimide. A potential route for the decomposition of **3** is via a homolytic β-scission reaction (Scheme 4). Support for this mechanism comes from drawing an analogy between **3** and *p*-toluenesulfonhydrazide, which decomposes in the presence of bases to yield diimide via a heterolytic β elimination[31] (Scheme 4).

The Φ_{acid}, Φ_{decomp}, and Φ_{ClSOH} values were determined under conditions of steady-state irradiation in O_2-saturated solutions. The results appear in Table 2. To interpret these results, one must appreciate that Φ_{PAG} is determined photometrically and, as a result, does not discriminate between different acids, whereas Φ_{ClSOH} is determined via HPLC and, hence, is selective for *p*-chlorobenzenesulfonic acid. The good agreement between Φ_{acid} and Φ_{ClSOH} indicates that the sulfonic acid is the only acid formed in any appreciable amount. This result indicates that, as expected, the SO_2 resulting from the desulfonylation reaction, as evidenced by the laser experiments, does not generate significant amounts of acid under these conditions. This result also suggests that **3** decomposes to give an arylsulfonyl radical that behaves in the same manner as the arylsulfonyl radical generated in the primary photochemical step, i.e., reaction with O_2 as the first step toward yielding a sulfonic acid.

Yet another confirmation that **3** decomposes to yield acid comes from the fact that Φ_{decomp} is smaller than Φ_{acid} and Φ_{ClSOH}. Clearly, this can only be the case if each PAG molecule is capable of decomposing to generate more than one acid molecule. Further, the fact that Φ_{acid} and Φ_{ClSOH} are double Φ_{decomp} indicates that, once formed, **3** decomposes essentially quantitatively to yield an arylsulfonyl radical.

It should also be noted from Table 2 that the Φ_{acid} value determined under steady-state conditions is approximately 4 times larger than the Φ_{acid} value determined by laser flash photolysis. This result was also encountered in the studies with **2a**–**d** and was attributed to the inherent differences between lamp and laser irradiation.[7] Briefly, laser excitation results in a greater concentration of reaction intermediates formed in the light path as compared to that formed by the much lower intensity lamps. The effect of this difference is that radical–radical recombination pathways, e.g.,

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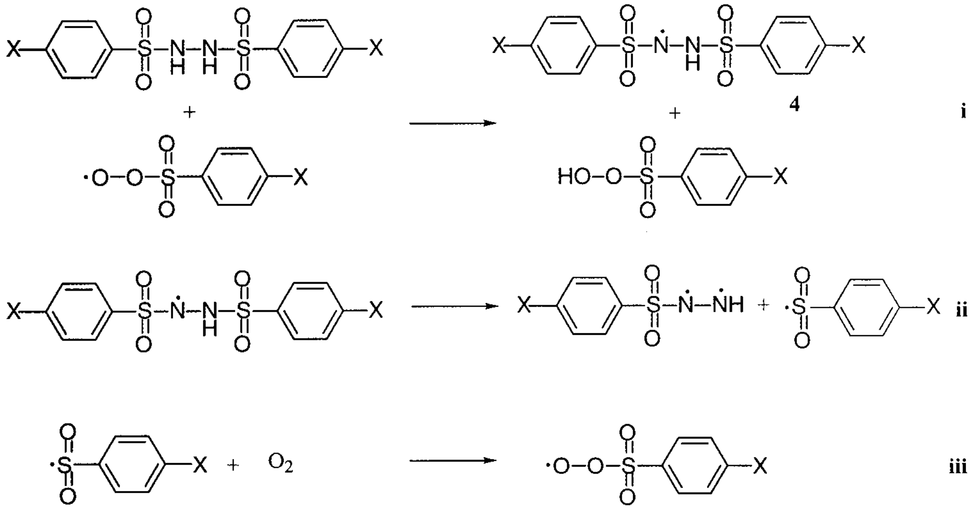
(30) Back, R. A. *Rev. Chem. Intermed.* **1984**, *5*, 293 and references therein.

(31) Gavina, F.; Luis, S. V.; Costero, A. M. *React. Polym.* **1987**, *6*, 291–298.

Scheme 5



reaction of arylsulfonyl with **3** to regenerate starting material, are able to compete much more effectively with other pathways that generate acid.

A process that, to this point, has not been discussed is the potential hydrogen-abstraction reaction between ground-state PAG molecules and oxygen-centered radicals produced in their photodecomposition to generate another nitrogen-centered radical (**4**) (reaction i, in Scheme 5). As indicated in Scheme 3, hydrogen abstraction from some substrate is a likely step in sulfonic acid formation. The behavior of *p*-toluenesulfonhydrazide as a hydrogen-atom donor has been established in reactions with *tert*-butoxy radicals and ^{3}XAN*, and it is reasonable to assume that **1a**−**d** will behave similarly. More interesting than this simple “induced decomposition” pathway is the possibility that, once **4** is formed, it will decompose in a manner similar to that observed in the case of the hydrazide and, in this way, generate acid. If this is the case, then there is the potential for involvement of a radical chain process in the acid generation of **1a**−**d**, the propagation steps of which appear in Scheme 5.

In a manner similar to that used with *p*-toluenesulfonhydrazide, the interaction of **1b** with ^{3}XAN* was studied. The hydrogen-atom-transfer process was again identified via the detection of the xanthone ketyl radical, and a rate constant of 8×10^8 M^{-1} s^{-1} was determined. To determine whether acid is generated after the formation of **4**, we irradiated xanthone at 350 nm in the presence of 0.021 M **1b** to quench more than 90% of the ^{3}XAN* formed. The results of the experiment appear in Figure 7, where it is shown that sensitized acid formation does occur when xanthone is excited in the presence of **1b**. This result indicates that **4** does decompose to yield acid, presumably in a manner similar to **3**. Interestingly, the yield of acid is approximately doubled when **1b**, which contains two arylsulfonyl moieties, is used as compared to *p*-toluenesulfonhydrazide, which contains only one. Given that conditions were chosen so that the efficiencies of sensitization were the same, this result seems to suggest that **4** decomposes quantitatively to generate two fragments containing the sulfonyl moiety. Reaction ii in Scheme 5 illustrates that a potential first step in this decomposition process is the loss of an arylsulfonyl radical. Although the specifics of this reaction are highly speculative, the generation of acid precursors of some kind from **4** is unquestionable.

Judging from the “model system” with xanthone and **1b**, in which hydrogen abstraction from the PAG was ensured, the reactions shown in Scheme 5 are all viable. However, their contributions to the direct photolysis of **1a**−**d** remain to be seen. To study this issue, Φ_{acid}, Φ_{decomp}, and Φ_{ClSOH} were again determined under conditions of steady-state irradiation in O_2-saturated solutions in the absence of 0.5 M diglyme as a hydrogen donor; although diglyme is only a modest hydrogen donor, this experiment is consistent with earlier work, in which chlorine atoms were involved. These results also appear in Table 2. In the absence of a hydrogen donor, the potential for interaction between species capable of hydrogen abstraction and ground-state PAG should increase, thereby resulting in increases in Φ_{acid}, Φ_{decomp}, and Φ_{ClSOH}. However, this effect is not observed, which suggests either that hydrogen abstraction from the PAG by reaction intermediates is not involved or that a competition with diglyme is not favorable. The source of hydrogen atoms in solution remains uncertain at this point.

In an attempt to bias the system in favor of interaction between the PAG and a species capable of hydrogen abstraction, we performed experiments in thin polymer films in which the PAG concentration was much higher than that in solution (5% w/w of polymer). Thin films of polymethyl methacrylate and either **1a** or **2a** were optically matched at 254 nm and irradiated. Acid generation was detected by extracting the film in a solution containing Rb as an acid sensor. **2a** was used as a model compound in which there is no possibility of a radical chain mechanism. The results reveal that the two PAGs have essentially the same Φ_{acid} value, which is in agreement with the fact that they have very similar values of Φ_{acid} in solution. We are forced to conclude that the radical chain pathway is again not active under the conditions employed. Apparently, hydrogen abstraction from the polymer matrix is favored over abstraction from the PAG. Interestingly, the indication that the ratio of Φ_{acid} in solution is retained in polymer films for a given set of PAGs with similar mechanisms for photodecomposition is a useful piece of information, as the determination of quantum yields in thin films is not trivial.

Conclusion

Irradiation of 1,2-di(arylsulfonyl)hydrazines leads to production of an arylsulfonyl radical and a nitrogen-centered radical. Laser flash photolysis indicates that the arylsulfonyl radical reacts with O_2 to form peroxysulfonyl radicals in competition with desulfonylation to generate SO_2 and aryl radicals. Steady-state irradiations indicate that the only acids generated are sulfonic acids, which are presumed to be the stable decomposition products of peroxysulfonic acids. Photoacid quantum yields upon laser excitation ranged from 0.05 to 0.1. Decomposition of the nitrogen-centered radical yields another arylsulfonyl radical, which is available for further acid generation.

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